Superposition model analysis for the zero-field splitting of Mn$^{2+}$ in Nd$_2$Mg$_3$(NO$_3$)$_{12}.24$H$_2$O

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**ABSTRACT**

The Newman superposition model has been applied to second-order zero-field splitting parameter $b_{20}$ for Mn$^{2+}$ in Nd$_2$Mg$_3$(NO$_3$)$_{12}.24$H$_2$O. It is shown that calculated value of $b_{20}$ is in agreement with the experimental value if local lattice relaxations are taken into account.

**KEYWORDS**

Superposition model; Electron paramagnetic resonance; Mn$^{2+}$; Zero-field splitting.

**INTRODUCTION**

Since the electron paramagnetic resonance (EPR) of S-state ions is easily detectable even at room temperature, many EPR investigations resulting in the determination of zero-field splitting (ZFS) parameters in single crystals have been reported in the literature. In most of these systems the S-state ions were coordinated by oxygen and the ZFS parameter $b_{20}$ is quite sensitive with respect to small structure changes. The calculations of ZFS follow two approaches. In the first, which is referred to as *ab-initio* calculation, the ZFS is generally calculated using an electrostatic model of the crystal field, together with one or more of the splitting mechanisms. The second method of estimating the ZFS is by the Newman empirical superposition model (SPM) relating the fine structure constants to the actual arrangements of ligands around the impurity[1]. The SPM has proved to be a very powerful tool in probing the local structure of S-state ions in a variety of compounds[2]. In particular, the method has been successfully applied to gain very detailed information on the lattice site and crystalline environment of Mn$^{2+}$ in a number of systems. This paper describes the SPM analysis of the trigonal spectra of Mn$^{2+}$ in Nd$_2$Mg$_3$(NO$_3$)$_{12}.24$H$_2$O (NMN) at room temperature. The EPR data have been taken from the literature[3] and the analysis is restricted to the largest ZFS parameter $b_{20}$.

**SUPERPOSITION MODEL**

The SPM is based on two assumptions: (i) the total ZFS experienced at an ion in a crystal is due to the close neighbour ions only and (ii) the ZFS at one ion caused by the second ion is intrinsic to that ion pair, i.e. is dependent upon exactly what ions are present and the distance between them, irrespective of the other surrounding. In the SPM, the total ZFS at the central ion is therefore given by a sum of axially symmetric contributions of the ligands i of MX$_1$ unit only. The contri-
butions of more distant neighbours as well as the interactions between the ligands are ignored[4]. Two sources of ZFS may be distinguished (i) contribution of the overlap and covalency and (ii) contribution of the crystal field. The former mechanism was shown to be superimposable as long as charge transfer and overlap remain small[4]. The analysis of the superimposability of the crystal field contribution to ZFS is very complicated. The SPM must hold for crystal field itself and second the spin-Hamiltonian parameter must be linear in crystal field. The analysis of the superimposability of the crystal field contribution to ZFS is very complicated. The SPM must hold for crystal field itself and second the spin-Hamiltonian parameter must be linear in crystal field. The main limitation in applying SPM is to determine exactly the position of the ligands, contribution to ZFS from next nearest Zn\(^{2+}\) and Ba\(^{2+}\). The primitive cell parameters for CMN are an = 1.1004 nm, c = 3.4592 nm. The rhombohedral unit cell contains three divalent ions situated at two different lattice sites. One occupies the C\(_{3v}\) point symmetry site (site I) and the other two occupy the C\(_3\) point symmetry site (site II). The divalent ions are surrounded by six water molecules forming a nearly octahedral complex. Each Nd\(^{3+}\) is coordinated with twelve oxygen ions belonging to six nitrate ions, located at the corners of a somewhat irregular icosahedron.

The EPR of Mn\(^{2+}\) in NMN shows the presence of two inequivalent Mn\(^{2+}\) centres of unequal intensity. The Mn\(^{2+}\) substitutes for Mg\(^{2+}\) and shows the spectrum of two Mn\(^{2+}\) complexes. It was found that the principal z axes of two [Mn(H\(_2\)O)\(_6\)]\(^{2+}\) complexes are along the c axis and x axis is perpendicular to the c axis. The zero-field splitting parameter \(b_0\) (D) of Mn\(^{2+}\) at site I and II are -171.2 x 10^{-4} cm\(^{-1}\) and 19.4 x 10^{-4} cm\(^{-1}\), respectively[3]. Mg\(^{2+}\) in NMN at site I is surrounded by six water molecules at a distance of 0.2058 nm. The detailed crystal structure of NMN has not been determined. However, it is expected that bond lengths of Mg\(^{2+}\)-H\(_2\)O in NMN would not be very different from that of Mg\(^{2+}\)-H\(_2\)O in CMN. In the SPM analysis the structural data of CMN is used. Mg\(^{2+}\) in NMN at site I is surrounded by six water molecules at a distance \(R = 0.2058\) nm and at site II is surrounded by two sets of three water molecules each as nearest neighbours at distances 0.2056 nm and 0.2058 nm[7]. The angle \(\theta\) that Mg-O makes with the c axis at site I is 54.10° and for site II are 54.83° and 123.69°. The calculated value of \(\theta\) is 54.10°.
of ZFS parameter $D$ is $-75.7 \times 10^{-4}$ cm$^{-1}$ and $104.8 \times 10^{-4}$ cm$^{-1}$. The SPM predicts the correct sign. The calculated value of $D$ for site I is smaller than the experimental value and larger for site II.

In these calculations, the assumption has been made that the crystalline structure in the vicinity of the magnetic ion is unchanged from those of the host lattice. The difference in calculated and experimental values of $D$ may be, in principle, due to local relaxation. It has been shown that if $R$ (metal-ligand bond distance) > normal Mn-ligand bond distance, the introduction of substitutional Mn$^{2+}$ gives rise to an inward relaxation while the opposite occurs for $R$ < Mn-ligand bond distance$^{[9]}$. The ionic radii of Mg$^{2+}$ and Mn$^{2+}$ are 0.066 nm and 0.080 nm$^{[8]}$. Therefore, Mn$^{2+}$ substitution for Mg$^{2+}$ would allow some expansion of O$_2^-$ octahedron around manganese. A movement of oxygen along the c axis is assumed such that Mn-oxygen bond length increases from that Mg-oxygen. This causes a change in the value of $\theta$. It is found that an increase of about 1.454% in bond lengths (from 0.2058 to 0.2088 nm) causes the angle $\theta$ to change to $53^0$ for site I. An increase of about 0.9% in bond length for site II causes $\theta$ to change to 54.33$^0$ and 124.33$^0$. These values of $R$ and $\theta$ leads to $b_{20}^0$ values -187 $\times$ 10$^{-4}$ cm$^{-1}$ and 19.5 $\times$ 10$^{-4}$ cm$^{-1}$ for site I and II respectively. A change of bond lengths of about 3%-4% is observed from EXAFS measurements in KZnF$_3$ and KCdF$_3$ doped with Mn$^{2+}$$^{[9]}$.

In conclusion, with the use of the SPM, it is possible to obtain the ZFS parameter $b_{20}^0$ for Mn$^{2+}$ in host lattice studied from crystal structure data by taking into account the local relaxation effects.

REFERENCES